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PREPARATION OF

NEW METHYLENEDIOXYPHENYL COMPOUNDS AND ACYLBENZALS

Growth Through Agricultural Progress

UNITED STATES DEPARTMENT OF AGRICULTURE
Agricultural Research Service

PREPARATION OF NEW METHYLENEDIOXYPHENYL COMPOUNDS AND ACYLBENZALS[1/]

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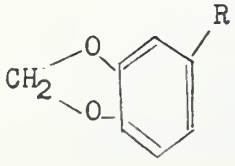
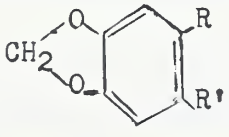
Interest in methylenedioxyphenyl compounds as pesticides and in acylbenzals as potential insect antifertility agents (and incidentally as anti-tumor agents) has led us to synthesize a number of new compounds of these types.

Because of the ease with which safrole (Ia) or isosafrole (Ib) can be hydrogenated, and the smooth conversion of the resultant compound, 1,2-methylenedioxy-4-propylbenzene, to 1,2-methylenedioxy-4-nitro-5-propylbenzene (II, R = C_3H_7; R' = NO_2) (Rayet et al. 23) and then to 4,5-methylenedioxy-2-propylaniline

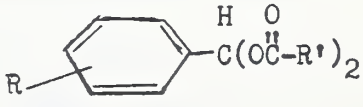


Ia, R = CH_2-CH=CH_2

b, R = CH=CH-CH_3



II



III

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1 Part of this paper is based upon the thesis submitted by T. A. Oda to the Graduate School of American University in partial fulfillment of the requirements for the Master of Science degree.

(II, R = C_3H_7; R' = NH_2) (Rayet et al. 23), we prepared some hitherto unknown methylendioxyaniline derivatives by this route. The nitro compound was obtained from 1,2-methylenedioxy-4-propylbenzene and nitric acid in 96 percent yield. Reduction of II (R = C_3H_7; R' = NO_2) with hydrogen and nickel-kieselguhr catalyst (Covert et al. 4) under pressure gave II (R = C_3H_7; R' = NH_2) in 84 percent yield. The amine thus produced was treated with various acid chlorides in the presence of pyridine and benzene to give new anilides.

Reaction of the amine with benzenesulfonyl chloride gave the crude 4',5'-methylenedioxy-2'-propylbenzenesulfonanilide (II, R = C_3H_7; R' = $NHSO_2C_6H_5$) in 90 percent yield. This anilide contained an impurity difficult to remove, and hence was characterized by methylation to N-methyl-4',5'-methylenedioxy-2'-propylbenzenesulfonanilide [II, R = C_3H_7; R' = $N(CH_3)$-$SO_2C_6H_5$] according to the procedure of Morgan and Micklethwait (18).

1-Piperonyl-1-bromoethane (Lieberman et al. 14) (II, R = H; R' = $CH_2CHBrCH_3$) was prepared but contrary to our expectation, attempts to replace the secondary bromo atom with the sulfhydryl group by general procedures described in the literature--i.e., using alcoholic thiourea (Urquhart et al. 26) or Bunte salts (Westlake and Dougherty 28)--were unsuccessful.

Attempts to prepare 4,5-methylenedioxy-2-propylbenzenethiol (II, R = C_3H_7; R' = SH) from II (R = C_3H_7; R' = NH_2) by diazotization (Miller and Read 17; Morgan and Cretcher 19) or from II (R = C_3H_7; R' = H) with chlorosulfonic acid (Hansch and Blondon 7) failed. However, the alpha halogen atom of 6-chloropiperonyl chloride (Naik and Wheeler 20; Barthel and Alexander 1) reacted readily with alcoholic thiourea (Urquhart et al. 26) to give 2-chloro-4,5-methylenedioxy-α-toluenethiol (II, R = Cl; R' = CH_2SH) in

76 percent yield. The melting point of the alpha-toluenethiol was not depressed when mixed with 6-chloropiperonyl chloride.

The procedure of Barthel and Alexander (1) for the preparation of 6-chloropiperonyl chloride at 50° was improved. A better product in higher yield was obtained by chlorinating piperonyl alcohol in glacial acetic acid at 20 to 25° (Dewey et al. 5) or at minus 60° with ether as the reaction solvent.

Treatment of the toluenethiol with sodium ethylate and ethylene chlorohydrin (Windus and Shildneck 29) gave 2-(6-chloropiperonyl)thioethanol (II, R = Cl; R' = $CH_2SC_2H_4OH$) in 73 percent or its bromo analog in 52 percent yield. The thioether-alcohols obtained were reacted with thionyl chloride (Kirner and Windus 12) and the "half-mustard gas" molecules (II, R = Cl or Br; R' = $CH_2SC_2H_4Cl$) were produced in 67 and 74 percent yields, respectively. The vesicant properties of these compounds, if any, were not ascertained.

The acylals, or more specifically acylbenzals (III), were prepared for tests as insect antifertility agents and anti-tumor agents. The general term "acylal" was coined by Hurd and Cantor (10) and Hurd and Green (11) in 1941, and although this class of compounds has been well known since the end of the nineteenth century along with its general method of synthesis (Skraup 24; Wegscheider and Späth 27), it is mentioned in few organic chemistry textbooks. A convenient method of preparing the acylbenzals is to allow the aldehyde to react with the appropriate acid anhydride in the presence of an acidic catalyst. For our purposes a small amount of sulfuric acid was employed successfully; however, boron fluoride may give higher yields (Man et al. 16).

Experimental

All degrees are Centigrade.

1,2-Methylenedioxy-4-propylbenzene (II, R = H, R' = C_3H_7). Safrole (162 g.), absolute ethanol (125 ml.), and nickel-kieselguhr (Covert et al. 4) catalyst (4 g.) were hydrogenated at 2000 p.s.i. of hydrogen at 25 to 50°; b.p. 112-113°/15 mm., n_D^{25} 1.5169; yield quantitative (Brochet and Bauer 2).

1,2-Methylenedioxy-4-nitro-5-propylbenzene (II, R = C_3H_7; R' = NO_2). 1,2-Methylenedioxy-4-propylbenzene was nitrated in the same manner as described for the nitration of 3,4-methylenedioxyphenyl acetate (Gertler et al. 6); m.p. 35-36° (90 percent ethanol)(Rayet et al. 23); yield 96 percent.

Anal. Calcd. for $C_{10}H_{11}NO_4$: C, 57.40; H, 5.30; N, 6.70. Found: C, 57.50; H, 5.26; N, 6.98.

4,5-Methylenedioxy-2-propylaniline (II, R = C_3H_7; R' = NH_2). The nitro compound (II, R = C_3H_7; R' = NO_2; 53 g.), absolute ethanol (70 ml.), and nickel-kieselguhr catalyst (6 g.) were hydrogenated with a 3 to 4 molar excess of hydrogen at 2000 p.s.i. and a temperature range of 70 to 105°. After the catalyst was removed, the solution colored rapidly to a dark red, apparently from air oxidation; b.p. 114°/0.4 mm. for 163-167°/20 mm., n_D^{25} 1.5619 (Rayet et al. 23); yield 84 percent.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.66; H, 7.30; N, 8.16.

N-(2'-Propyl-4',5'-methylenedioxyphenyl)chrysanthemumamide (II, R = C_3H_7; R' = $NHC(=O)-C(H)-C(H)(C(CH_3)_2)-C(H)=C(CH_3)_2$). The amine (II, R = C_3H_7; R' = NH_2; 0.7 mole or 126 g.), dry benzene (800 ml.), and dry pyridine (82 ml.) were stirred at 25°. Chrysanthemumoyl chloride (Chen and Barthel 3) (0.7 mole or 130 g.) was slowly added to the solution without cooling of the exothermic reaction.

After the addition, stirring was continued for several hours, and the product was allowed to stand overnight at 25°.

The benzene mixture was washed with water, dilute hydrochloric acid, water, and a saturated sodium chloride solution. Removal of the benzene left the crude amide in crystalline form. Three recrystallizations from ethanol did not alter its melting point significantly; m.p. 106-110°; yield 65 percent. The chrysanthemumoyl chloride starting material was a cis-trans mixture, and undoubtedly the product was a similar mixture; hence our inability to get a sharp melting point.

Anal. Calcd. for $C_{20}H_{27}NO_3$: C, 72.91; H, 8.26; N, 4.25. Found: C, 72.99; H, 8.02; N, 4.77.

2-Phenyl-N-(2'-propyl-4',5'-methylenedioxyphenyl)acetamide (II, R = C_3H_7; R' = $NHCOCH_2C_6H_5$) was prepared as described above from 4,5-methylenedioxy-2-propylaniline (75 g.), benzene (700 ml.), dry pyridine (55 ml.), and phenylacetyl chloride (65 g.); m.p. 145-146° (ethanol); yield 78 percent. This compound was characterized by making its N-methyl derivative, which is described later.

Anal. Calcd. for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44. Found: C, 71.62; H, 6.40.

4',5'-Methylenedioxy-2'-propylbenzenesulfonanilide (II, R = C_3H_7; R' = $NHSO_2C_6H_5$) was prepared in the usual way from 0.7-mole quantities, of the amine (II, R = C_3H_7; R' = NH_2), aqueous sodium hydroxide, and bensenesulfonyl chloride; m.p. 187-190° (dec.). Two recrystallizations from ethanol and one from methanol failed to give a pure product; yield 90 percent. It was therefore characterized by its N-methyl derivative, the preparation of which is described below.

Anal. Calcd. for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.37. Found: C, 57.98; H, 5.09.

N-Methyl-4',5'-methylenedioxy-2'-propylbenzenesulfonanilide [II, R = C_3H_7; R' = $N(CH_3)SO_2C_6H_5$]. The crude sulfonanilide above (0.16 mole), absolute ethanol (400 ml.), and sodium hydroxide (0.16 mole) were refluxed for about 2 hours and then methyl iodide (0.3 mole) was slowly added to the refluxing solution (Morgan and Micklethwait 18); the mixture was refluxed for 14 additional hours and then allowed to stand over the weekend. The alcohol was removed by heating the product on a steam bath, and the residue was poured into cold water. The product was extracted with ether, and the ether layer washed with dilute hydrochloric acid, saturated sodium bicarbonate, water, and finally with saturated sodium chloride solution. When the ether was removed, crystallization occurred; m.p. 102-103° (ethanol): yield 90 percent.

Anal. Calcd. for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74. Found: C, 61.43; H, 5.84.

N-Methyl-2-phenyl-N-(4',5'-methylenedioxy-2'-propylphenyl)acetamide (II, R = C_3H_7; R' = $N(CH_3)COCH_2C_6H_5$). The reaction product of the crude amide (II, R = C_3H_7; R' = $NHCOCH_2C_6H_5$; 0.074 mole), dry toluene (150 ml.), and pieces of sodium metal (0.085 gram-atom) was treated with methyl iodide under reflux conditions and worked up essentially as described above to give the desired product; m.p. 144-145° (ethanol); yield 11 percent.

Anal. Calcd. for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80. Found: C, 73.16; H, 6.43.

N-Methyl-N-(4',5'-methylenedioxy-2'-propylphenyl)chrysanthemumamide [II, R = C_3H_7; R' = $N(CH_3)\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=C(CH_3)_2$ with $C(CH_3)_2$ bridge]. The reaction product of

[II, R = C_3H_7; R' = $NH\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=C(CH_3)_2$ with $C(CH_3)_2$ bridge; 0.185 mole], dry toluene (200 ml.), and

sodium metal (0.22 gram-atom) was treated as described above with methyl iodide (0.6 mole); b.p. 158-160°/0.3 mm., n_D^{25} 1.5313; yield 86 percent. The product was a mixture of cis and trans isomers.

Anal. Calcd. for $C_{21}H_{29}NO_3$: C, 73.43; H, 8.51. Found: C, 73.20, H, 8.88.

6-Chloropiperonyl p-chlorophenoxyacetate (II, R = Cl; R' = $CH_2OCCH_2OC_6H_4Cl$). 6-Chloropiperonyl alcohol (Naik and Wheeler 20) (0.37 mole), dry benzene (250 ml.), dry pyridine (50 ml.), and p-chlorophenoxyacetyl chloride (Wood and Fontaine 30) (0.37 mole) were reacted in the usual way; m.p. 87-88° (ethanol); yield 60 percent.

Anal. Calcd. for $C_{16}H_{12}Cl_2O_5$: C, 54.10; H, 3.41; Cl, 19.97. Found: C, 53.70; H, 3.86; Cl, 20.15.

6-Bromo-α-(1-morpholinoethyl)piperonyl alcohol (II, R = Br, R' = $CHOHCH(CH_3)N(CH_2CH_2)_2O$). 4-Bromo-5-(1',2'-epoxypropyl)-1,2-methylenedioxybenzene [II, R = Br, R' = $CH\text{-}CH\text{-}CH_3$ (Höring 9; Pond et al. 21; Pond and Siegfried 22; Hoering 8); 0.3 mole)] and freshly distilled morpholine (0.4 mole) were mixed and heated under reflux conditions at a bath temperature of 140-146° for 3 hours in accordance with directions already described (Krassusky and Kussner 13; Lutz et al. 15); m.p. 126-127° (benzene, then aqueous methanol); yield 30 percent.

Anal. Calcd. for $C_{14}H_{18}BrNO_4$: C, 48.85; H, 5.27; N, 4.07. Found: C, 48.50; H, 5.54; N, 4.42.

6-Chloropiperonyl chloride (II, R = Cl, R' - CH_2Cl). Procedure A (Dewey et al. 5): A 3-liter, 3-necked, r.b. flask was equipped with a mechanical stirrer, a gas-inlet tube, a thermometer, and a reflux condenser topped with a dry-ice trap. The exit tube was connected to a bubble counter

containing glacial acetic acid. The flask was charged with 380 g. (2.5 mole) of piperonyl alcohol in 1000 ml. of glacial acetic acid and cooled in a salt-ice bath. The gas-inlet tube was connected to a bottle containing 185 g. (2.6 mole) of liquid chlorine. As it warmed, chlorine gas was passed into the stirred contents of the reaction flask at such a rate that no gas escaped through the bubble counter and the reaction temperature was maintained between 20 and 25°. After the chlorine had been added (2 hours), the mixture was stirred an additional hour and the acetic acid was removed in vacuo; m.p. 62-65° (methanol). Stripping and rapid distillation of the mother liquors through a short modified Claisen head gave more product; total yield was 71-87 percent (several crops).

Procedure B: This procedure was simpler and gave a higher yield: A 4-liter beaker containing piperonyl alcohol (1.4 mole) in ether (2000 ml.) was immersed in a dry ice-acetone bath and stirred vigorously with an air stirrer. The alcohol precipitated out in tiny crystals as the temperature fell to minus 60°. At this temperature liquid chlorine (63.7 ml. or 1.4 mole) was carefully added. The temperature rose to minus 20° and the solid particles dissolved. After several minutes a thick solid suspension formed. The mixture was diluted with an additional 500 ml. of ether and stirred for 3 hours at minus 60°, and then left standing at room temperature overnight in the hood. The product, which was then a clear yellow solution, was washed with water, saturated sodium bicarbonate solution, and twice with saturated sodium chloride solution. After removal of the ether, the residue solidified as light-brown crystals; weight 258 g. (1.3 moles); m.p. of crude material 62-65°; yield 90 percent (first crop).

2-Chloro-4,5-methylenedioxy-α-toluenethiol (II, R = Cl, R' = CH_2SH) was prepared from 6-chloropiperonyl chloride (0.85 mole), thiourea (0.85 mole), and 95 percent ethanol (425 ml.) by described procedures (Urquhart et al. 26); m.p. 62-63° (95 percent ethanol); oddly enough, the melting point was not changed when the compound was mixed with 6-chloropiperonyl chloride; yield 76 percent.

Anal. Calcd. for $C_8H_7ClO_2S$: C, 47.41; H, 3.48. Found: C, 47.33; H, 3.73.

6-Chloropiperonyl thiolacetate (II, R = Cl, R' = $CH_2S\overset{O}{\overset{\|}{C}}CH_3$) was prepared in the usual way from the above thiol (5 g.), acetic anhydride (30 ml.), and 4 drops of concentrated sulfuric acid; m.p. 103-104° (ethanol); yield quantitative.

Anal. Calcd. for $C_{10}H_9ClO_3S$: C, 49.08; H, 3.71. Found: C, 48.92; H, 3.97.

6-Chloropiperonyl methyl sulfide (II, R = Cl, R' = CH_2SCH_3) was prepared from II (R = Cl, R' = CH_2SH; 0.2 mole), aqueous 10 percent sodium hydroxide (100 ml.), and dimethyl sulfate (0.22 mole) according to reported procedures (Tarbell and Fukushima 25); b.p. 96-103°/0.3 mm., n_D^{25} 1.5911; yield 74 percent.

Anal. Calcd. for $C_9H_9ClO_2S$: C, 49.88; H, 4.19. Found C, 49.63; H, 4.27.

2-(6-Chloropiperonylthio)ethanol (II, R = Cl, R' = $CH_2SC_2H_4OH$) was prepared from II (R = Cl, R' = CH_2SH; 0.19 mole), sodium (0.35 gram-atom), dry ethanol (150 ml.), and ethylene chlorohydrin (0.38 mole) by the procedure of Windus and Shildneck (29); b.p. 151-159°/0.3 mm., n_D^{25} 1.5971; yield 73 percent.

Anal. Calcd. for $C_{10}H_{11}ClO_3S$: C, 48.68; H, 4.49. Found: C, 48.34, H, 4.63.

2-Chloroethyl 6-chloropiperonyl sulfide (II, R = Cl. R' = $CH_2SC_2H_4Cl$) was prepared from the above thioethanol (II, R = Cl; R' = $CH_2SC_2H_4OH$: 0.13 mole), dry benzene (200 ml.), and thionyl chloride (0.14 mole) by the procedure of Kirner and Windus (12); b.p. 128-138°/0.3 mm., n_D^{25} 1.5955; yield 67 percent.

Anal. Calcd. for $C_{10}H_{10}Cl_2O_2S$: C, 45.29; H, 3.80. Found: C, 45.34; H, 3.89.

2-(6-Bromopiperonylthio)ethanol (II, R = Br, R' = $CH_2SC_2H_4OH$) was prepared in a manner analogous to the chlorinated compound from 2-bromo-4,5-methylenedioxy-α-toluenethiol; b.p. 155-156°/0.2 mm., n_D^{25} 1.6162; yield 52 percent.

Anal. Calcd. for $C_{10}H_{11}BrO_3S$: C, 41.25; H, 3.81. Found: C, 41.57; H, 4.20.

6-Bromopiperonyl 2-chloroethyl sulfide (II, R = Br; R' = $CH_2SC_2H_4Cl$) was prepared in the same way as the corresponding chloro analog above; b.p. 130-147°/0.3 mm., n_D^{25} 1.6121; yield 74 percent.

Anal. Calcd. for $C_{10}H_{10}BrClO_2S$: C, 38.79; H, 3.26. Found: C, 39.07; H, 3.54.

Synthesis of Acylbenzals (III). All these compounds were prepared in essentially the same manner (Skraup 24; Wegscheider and Spath 27; Man et al 16; Hurd and Green 11; Hurd and Cantor 10). A typical experiment follows: The aldehyde (0.3 mole) and acetic anhydride (100 ml. except for phenolic aldehydes, i.e., hydroxybenzaldehydes, for which 200 instead of 100 ml. was used, because the phenolic hydroxy group was also acylated in the process) were stirred at 25°, and 1 ml. of concentrated sulfuric acid was added. The reaction mixture became warm, and was given a minimal amount of cooling only when the temperature rose above 84°. When the initial reaction subsided, the mixture was usually stirred for 1 hour and allowed to stand overnight. It was then poured into cold water. In some cases, a crystalline

product was obtained; in others, an oil separated. Whenever the oil formed, it was taken up in ether and the ether layer washed with saturated sodium bicarbonate solution, dried, the solvent removed, and the residue distilled. Physical constants, yield, and elemental analyses are given in table 1.

Our acylbenzals, like those reported by Wegscheider and Spath (27) and Skraup (24) give positive tests with phenylhydrazine and 2,4-dinitrophenylhydrazine.

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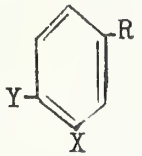
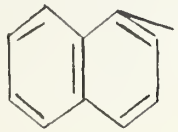
Table 1.--Physical constants, yields, and analytical data for acylbenzals



$R_1 = -CH(O\overset{O}{\overset{\|}{C}}CH_3)_2$ $R_2 = -CH(O\overset{O}{\overset{\|}{C}}C_2H_5)_2$ $R_3 = -CH(O\overset{O}{\overset{\|}{C}}C_3H_7)_2$

R	X	Y	Yield (%)	B.P.°C/ (mm.)	n_D^{25} or m.p.	Formula	Analysis			
							Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found
R_2	H	$-OCOCH_3$	80	139-143/0.2	1.4864	$C_{15}H_{18}O_6$	61.22	60.84	6.17	6.11
R_3	H	$-OCOCH_3$	80	149-152/0.3	1.4815	$C_{17}H_{22}O_6$	63.34	63.46	6.88	7.13
R_2	$-OCOC_2H_5$	H	74	137-140/0.2	1.4844	$C_{16}H_{20}O_6$	62.32	62.47	6.54	6.38
R_3	$-OCOC_2H_5$	H	74	139-150/0.2	1.4795	$C_{18}H_{24}O_6$	64.27	64.01	7.19	7.21
R_1	H	$-OCOC_2H_5$	96	--	79-80°1/	$C_{14}H_{16}O_6$	59.99	60.84	5.76	6.33 2/
R_1	$-OCOC_2H_5$	H	83	131-135/0.2	1.4897	$C_{14}H_{16}O_6$	59.99	59.42	5.76	5.81
R_2	H	$-CH(CH_3)_2$	66	115-119/0.3	1.4836	$C_{16}H_{22}O_4$	69.04	68.56	7.97	7.93
R_2	$-OCH_3$	$-OCOC_2H_5$	38	153-162/0.5	1.4910	$C_{17}H_{22}O_7$	60.34	60.54	6.56	6.81
$-CH(CH_3)-R_1$	H	H	42	80-98/0.2	1.4906	$C_{13}H_{16}O_4$	66.08	65.90	6.83	6.71
 $CH(OCOCH_3)_2$			69	--	108°1/	$C_{15}H_{14}O_4$	69.76	69.45	5.46	5.61

1/ From aqueous ethanol.

2/ Unable to obtain better carbon and hydrogen analyses even after a sharp melting point was obtained.